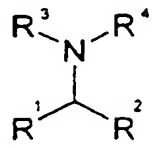
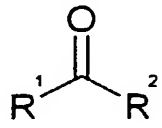
Claims

1. A process for preparing amines of the formula (III)



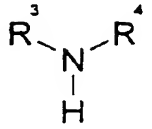
(III)

by reacting a compound of the formula (I)



(I)

with a compound of the formula (II)



(II)

where the radicals

R^1 to R^4 are selected independently from the group consisting of hydrogen, (C_1-C_{24})-alkyl, (C_2-C_{24})-alkenyl, (C_2-C_{24})-alkynyl, (C_6-C_{10})-aryl, CF_3, CN, COOH, COOM, where M is a cation selected from the group consisting of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, $N(C_1\text{-}C_{10}\text{-alkyl})_4^+$, $N(C_1\text{-}C_{10}\text{-alkyl}/C_6\text{-}C_{10}\text{-aryl})_4^+$, CHO, SO_3H, COO-alkyl-(C_1-C_8), $CONH_2$, CONHalkyl-(C_1-C_8), $CONalkyl_2$-(C_1-C_8), CO-alkyl-(C_1-C_8), CO-phenyl, COO-phenyl, COO-aryl-(C_6-C_{10}), CO-aryl-(C_6-C_{10}), $P(aryl)_2$, $Palkyl_2$-(C_1-C_8), $PO(aryl)_2$, $POalkyl_2$-(C_1-C_4), PO_3H_2, POalkyl-(C_1-C_4)(O-alkyl-(C_1-C_6)), PO(O-

alkyl-(C_1-C_6))$_2$, SO_3-alkyl-(C_1-C_4), SO_2-alkyl-(C_1-C_6), SO-alkyl-(C_1-C_6) or Si(alkyl)$_3$-(C_1-C_8), and/or R^3 and R^4 are selected independently from the group consisting of O-alkyl-(C_1-C_8), OCO-alkyl-(C_1-C_8), O-aryl, fluorine, OH, NH_2, NH-alkyl-(C_1-C_8), N-alkyl$_2$-(C_1-C_8), NHCO-alkyl-(C_1-C_4), NHCOO-alkyl-(C_1-C_4), NHaryl-(C_6-C_{10}),

where alkyl is, for the purposes of the present invention, an unbranched or branched aliphatic or cyclic radical, where from one to four carbon atoms of the alkyl radical may be replaced by nitrogen, sulfur or oxygen atoms, alkenyl is an olefinic hydrocarbon, alkynyl is an acetylenic hydrocarbon and aryl is an aromatic radical, where from one to four carbon atoms of the aromatic radical may be replaced by nitrogen, sulfur or oxygen atoms,

alkyl, alkenyl, alkynyl and also aryl may bear substituents selected independently from among hydrogen, O-alkyl-(C_1-C_8), OCO-alkyl-(C_1-C_8), O-phenyl, phenyl, aryl(C_6-C_{10}), fluorine, chlorine, bromine, iodine, OH, NO_2, CF_3, CN, COOH, COOM, where M is a cation selected from the group consisting of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, N(C_1-C_{10}-alkyl)$_4^+$, N(C_1-C_{10}-alkyl/C_6-C_{10}-aryl)$_4^+$, CHO, SO_3H, NH_2, NH-alkyl-(C_1-C_8), N-alkyl$_2$-(C_1-C_8), NHCO-alkyl-(C_1-C_4), COO-alkyl-(C_1-C_8), $CONH_2$, CO-alkyl-(C_1-C_8), NHCOH, NHCOO-alkyl-(C_1-C_4), CO-phenyl, COO-phenyl, COO-aryl-(C_6-C_{10}), CO-aryl-(C_6-C_{10}), CHCH-CO_2-alkyl-(C_1-C_8), P(aryl)$_2$, $CHCHCO_2H$, P-alkyl$_2$-(C_1-C_8), PO-aryl$_2$, POalkyl$_2$-(C_1-C_4), PO_3H_2, POalkyl-(C_1-C_4)(O-alkyl-(C_1-C_6)), PO(O-alkyl-(C_1-C_6))$_2$, SO_3-alkyl-(C_1-C_4), SO_2-alkyl-(C_1-C_6), SO-alkyl-(C_1-C_6) or Si(alkyl)$_3$-(C_1-C_8),

both R^1 and R^2 and also R^3 and R^4 can be linked by covalent bonds so that R^1 and R^2 and/or R^3 and R^4 in each case form a four- to eight-membered ring, where R^1 or R^2 may also be part of an organometallic compound,

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in the presence of hydrogen and a homogeneous catalyst system comprising at least one metal atom selected from the group consisting of Rh, Ru, Ir, Pd, Pt, Co and Ni and one or more monodentate or bidentate achiral or chiral ligands of the formula (IV) or (V)

$$(R^6Y^1)(R^7Y^1)P^1X^1ZX^2P^2(Y^2R^8)(Y^2R^9) \quad (IV)$$

$$(R^6Y^1)(R^7Y^1)(R^8Y^1)P \quad (V)$$

where

R^6 to R^9 are identical or different and are each a hydrogen atom, C_1-C_{24}-alkyl, C_2-C_{20}-alkenyl, C_3-C_8-cycloalkyl, C_5-C_8-cycloalkenyl, C_6-C_{14}-aryl, phenyl, naphthyl, fluorenyl, C_2-C_{13}-heteroaryl, where the number of heteroatoms from the group consisting of N, O, S can be 1-4,

and in which all the abovementioned substituents may each be substituted by one or more substituents selected independently from among hydrogen, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_1-C_{10}-haloalkyl, C_3-C_8-cycloalkyl, C_5-C_8-cycloalkenyl, C_2-C_9-heterocycloalkyl, C_1-C_9-heterocycloalkenyl, C_6-C_{14}-aryl, phenyl, C_2-C_{13}-heteroaryl, where the number of heteroatoms from the group consisting of N, O, S can be 1-4, C_1-C_{10}-alkoxy, OCO-alkyl-(C_1-C_8), O-aryl-(C_5-C_{10}), O-phenyl, C_1-C_9-trihalomethylalkyl, fluoro, chloro, bromo, iodo, nitro, hydroxy, trifluoromethylsulfonato, oxo, thio, thiolato, amino, C_1-C_8-substituted amino of the types mono- and di-C_1-C_8-alkylamino or C_2-C_8-alkenylamino or mono-, di-, tri-C_6-C_8-arylamino or C_1-C_8-alkyl-C_6-C_8-arylamino, NH-CO-alkyl-C_1-C_8, NH-CO-aryl-C_6-C_8, cyano, C_1-C_8-acyloxy, carboxyl, carboxylato of the formula $COOR^{12}$, sulfinato, sulfonato of the formula SO_3R^{12}, phosphonato of the formula PO_3H_2, PO_3HR^{12}, $PO_3R^{12}{}_2$, where R^{12} is either a monovalent cation, NH_4^+, $N(C_1\text{-}C_{10}\text{-alkyl})_4^+$, $N(C_1\text{-}C_{10}\text{-alkyl/}C_6\text{-}C_{10}\text{-aryl})_4^+$, C_1-C_{18}-alkyl or C_6-aryl, tri-C_1-C_6-alkylsilyl,

and where two of these substituents may also be bridged,

X^1 and X^2 are each, independently of one another, a direct phosphorus-carbon bond, O, S or NR^{10}, where

R^{10} corresponds to one of the radicals defined for R^6-R^9,

Y^1 and Y^2 is a direct phosphorus-carbon bond, -O- or -NR^{11}-, where

R^{11} corresponds to one of the radicals defined for R^6-R^9,

Z corresponds to 1-6 carbon atoms which are bound to one another by single or multiple bonds and connect the unit $(R^6Y^1)(R^7Y^1)PX^1$ to the unit $X^2P(Y^2R^8)(Y^2R^9)$, where Z may be part of an aliphatic, cycloaliphatic, olefinic, cycloolefinic system which may contain from one to four heteroatoms from the group consisting of N, O, S, a metallocene, in particular a ferrocene, a 1,1'-disubstituted ferrocene, 1-(1-ethylenyl)-2-ferrocenyl or a 1,2-disubstituted ferrocene, or one or more aromatic or heteroaromatic ring systems, where the ring system comprises a total of from 2 to 14 carbon atoms which may be monosubstituted or polysubstituted by substituents as specified for R^6-R^9 or directly by C_1-C_{10}-alkoxy, OCO-alkyl-(C_1-C_8), O-aryl-(C_5-C_{10}), O-phenyl, C_1-C_9-trihalomethylalkyl, trifluoromethyl, trichloromethyl, fluoro, chloro, bromo, iodo, nitro, hydroxy, trifluoromethylsulfonato, oxo, thio, thiolato, amino, C_1-C_8-substituted amino of the formulae NH_2, NH-alkyl-C_1-C_8, NH-aryl-C_5-C_6, N-alkyl$_2$-C_1-C_8, N-aryl$_2$-C_5-C_6, N-alkyl$_3$-C_1-C_8^+, N-aryl$_2$-C_5-C_6-aryl-C_5-C_6^+, C_1-C_6-acyloxy, carboxylato of the formulae COOH and $COOR^{12}$, sulfinato, sulfonato of the formulae SO_3H and SO_3R^{12}, phosphonato of the formulae PO_3H_2, PO_3HR^{12} and $PO_3R^{12}_2$, where R^{12} is either a monovalent cation, NH_4^+, $N(C_1$-C_{10}-alkyl$)_4^+$, $N(C_1$-C_{10}-alkyl/C_6-C_{10}-aryl$)_4^+$, C_1-C_8-alkyl or C_6-aryl, C_1-C_6-trialkylsilyl, NHCO-alkyl-(C_1-C_4), COO-alkyl-(C_1-C_8), $CONH_2$, CON(alkyl-(C_1-C_8))$_2$, CO-alkyl-(C_1-C_8), CO-alkenyl-(C_1-C_8), NHCOO-alkyl-(C_1-C_4), CO-aryl-(C_6-C_{10}), CO-phenyl, COO-aryl-(C_6-C_{10}), COO-phenyl, CHCH-CO_2-alkyl-(C_1-C_8), $CHCHCO_2H$, and

P is a trivalent phosphorus atom.

2. The process as claimed in claim 1, wherein bidentate ligands of the formula (IV) in which R^6 to R^9 are, independently of one another, C_1-C_8-alkyl, C_5-C_6-cycloalkyl, C_6-aryl, C_4-C_5-heteroaryl, where the number of heteroatoms is 1-2, selected from the group consisting of N, O, S, and the ring size is 5-6, or are naphthyl, with these groups being able to be bear one or more substituents, preferably

substituents selected independently from among hydrogen, C_1-C_{10}-alkyl, C_1-C_6-haloalkyl, C_5-C_6-cycloalkyl, C_2-C_9-heterocycloalkyl, C_6-aryl, phenyl, C_4-C_5-heteroaryl, where the number of heteroatoms from the group consisting of N, O, S, can be 1-2, C_1-C_6-alkoxy, OCO-alkyl-(C_1-C_6), O-aryl-C_6, C_1-C_6-trihalomethylalkyl, fluoro, chloro, bromo, iodo, nitro, hydroxy, oxo, thio, thiolato, amino, C_1-C_8-substituted amino of the types mono-, di-, tri-C_1-C_8-alkylamino or C_2-C_8-alkenylamino or mono- and di-C_6-C_8-arylamino or C_1-C_8-alkyl-C_6-C_8-arylamino, NH-CO-alkyl-C_1-C_8, NH-CO-aryl-C_6-C_8, C_1-C_8-acyloxy, carboxyl, carboxylato of the formula $COOR^{12}$, sulfinato, sulfonato of the formula SO_3R^{12}, phosphonato of the formula PO_3H_2, PO_3HR^{12}, $PO_3R^{12}{}_2$, where R^{12} is either a monovalent or divalent cation (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}), NH_4^+, $N(C_1$-C_{10}-alkyl$)_4^+$, $N(C_1$-C_{10}-alkyl/C_6-C_{10}-aryl$)_4^+$, C_1-C_8-alkyl or C_6-aryl, and tri-C_1-C_6-alkylsilyl, are used.

3. The process as claimed in either of the preceding claims, wherein R^6 to R^9 are selected independently from the group consisting of (C_3-C_8)-alkyl, (C_6-C_{10})-aryl, O-(C_5-C_8)-alkyl, O-(C_6-C_{10})-aryl or an aliphatic or aromatic (C_3-C_9)-heterocycle containing from 1 to 4 nitrogen atoms.

4. The process as claimed in any of the preceding claims, wherein R^6 and R^7 and/or R^8 and R^9 may be linked by a covalent bond so as to form a cyclic compound having from four to eight atoms.

5. The process as claimed in claim 1 or 2, wherein ligands in which Y^1 and Y^2 are each a direct phosphorus-carbon bond are used.

6. The process as claimed in any of the preceding claims, wherein Z comprises from one to four carbon atoms, in particular two carbon atoms.

7. The process as claimed in any of the preceding claims, wherein Z is a C_1-C_6-alkyl or C_2-C_6-alkenyl group or is part of a C_3-C_8-cycloalkyl, C_5-C_8-cycloalkenyl, C_2-C_9-heterocycloalkyl, C_1-C_9-heterocycloalkenyl, C_6-C_{14}-aryl, phenyl, naphthyl, fluorenyl or C_2-C_{13}-heteroaryl group, where the number of heteroatoms from the

group consisting of N, O, S can be 1-4 and all these groups may be monosubstituted or polysubstituted as described in claim 1.

8. The process as claimed in any of the preceding claims, wherein ligands in which a three- to nine-membered ring system can be formed by Z, X^1, X^2, P^1 and P^2 together with a coordinated metal are used.

9. The process as claimed in claim 1, wherein 1,4-bis(diphenylphosphino)butane, 1,4-bis(dicyclohexylphosphino)-butane, 2-diphenylphosphinomethyl-4-diphenylphosphino-1-tert-butoxycarbonylpyrrolidine, 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, (2*R*,3*R*,5*R*,6*R*)-2,3-dimethoxy-2,3-dimethyl-5,6-bis(diphenylphosphinomethyl)-1,4-dioxane, tris-(3-sulfophenyl)phosphine trisodium salt, 2,2'-bis[[bis(3-sulfophenyl)phosphino]methyl]-4,4',7,7'-tetrasulfo-1,1'-binaphthyl octasodium salt, diphosphinite ligands based on carbohydrates, 1,2-bis(diphenylphosphinoxy)ethane, (1*R*,2*R*)-(trans)-1,2-bis-(diphenylphosphinoxy)cyclohexane, (2*R*)-1-[[(diphenylphosphino)(cyclopenthyl)amino]methyl]-2-diphenylphosphinoxy-3-(1-naphthalenyloxy)propane and/or (4*S*)-2-(2-(diphenylphosphino)phenyl)-4-isopropyl-1,3-oxazoline are used as ligands.

10. The process as claimed in any of the preceding claims, wherein the starting materials of the formulae (I) and/or (II) used are ones whose substituents R^1 to R^4 are each, independently of one another, hydrogen, (C_1-C_{12})-alkyl, (C_2-C_{12})-alkenyl, (C_2-C_{12})-alkynyl, (C_6-C_{10})-aryl, CF_3, CN, COOH, COOM, where M is a cation selected from the group consisting of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, $N(C_1-C_{10}\text{-alkyl})_4^+$, $N(C_1-C_{10}\text{-alkyl}/C_6-C_{10}\text{-aryl})_4^+$, COO-alkyl-$(C_1-C_8)$, $CONH_2$, CONHalkyl-(C_1-C_8), CONalkyl$_2$-(C_1-C_8), CO-alkyl-(C_1-C_8), CO-phenyl, COO-phenyl, COO-aryl-(C_6-C_{10}), CO-aryl-(C_6-C_{10}), PO(aryl-$C_6-C_{10})_2$, POalkyl$_2$-(C_1-C_4), PO_3H_2, PO(alkyl-(C_1-C_4))(Oalkyl-(C_1-C_4)), PO(O-alkyl-(C_1-C_6))$_2$ or Si(alkyl)$_3$-(C_1-C_8) and/or R^3 and R^4 are selected independently from the group consisting of O-alkyl-(C_1-C_8), OCO-alkyl-(C_1-C_8), O-aryl(C_6-C_{10}), OH, NH_2, NH-alkyl-(C_1-C_8), N-alkyl$_2$-(C_1-C_8), NHCO-alkyl-(C_1-C_4), NHCOO-alkyl-(C_1-C_4), NHaryl-(C_6-C_{10}), where alkyl is

an unbranched or branched aliphatic or cyclic or heterocyclic radical containing from one to four heteroatoms selected from the group consisting of N, O, alkenyl is an olefinic hydrocarbon, alkynyl is an acetylenic hydrocarbon and aryl is an aromatic radical which may also be an aromatic containing 1-4 heteroatoms from the group consisting of N, O and S,
and alkyl, alkenyl and alkynyl and also aryl may bear substituents selected independently from among hydrogen, O-alkyl-(C_1-C_8), OCO-alkyl-(C_1-C_8), O-phenyl, phenyl, aryl-C_6-C_{10}, fluorine, chlorine, bromine, iodine, OH, NO_2, Si-alkyl$_3$-(C_1-C_8), CF_3, CN, COOH, COOM, where M is a monovalent cation selected from the group consisting of Na, K, Rb, Cs, NH_4, N(C_1-C_{10}-alkyl)$_4$, N(C_1-C_{10}-alkyl/C_6-C_{10}-aryl)$_4$, and SO_3H, N-alkyl$_2$-(C_1-C_8), SO_2-alkyl-(C_1-C_6), SO-alkyl-(C_1-C_6), NHCO-alkyl-(C_1-C_4), COO-alkyl-(C_1-C_8), $CONH_2$, CO-alkyl-(C_1-C_8), CO-phenyl, COO-phenyl, COO-aryl-(C_6-C_{10}), CO-aryl-(C_6-C_{10}), PO-phenyl$_2$, POalkyl$_2$-(C_1-C_4), PO_3H_2, POalkyl-(C_1-C_4)(O-alkyl-(C_1-C_6)), PO(O-alkyl-(C_1-C_6))$_2$, Si(alkyl)$_3$-(C_1-C_8), where alkyl and aryl are as defined above.

11. The process as claimed in any of the preceding claims, wherein the starting materials of the formulae (I) and/or (II) used are ones in which R^1 and R^2 and/or R^3 and R^4 are linked by covalent bonds so as to form a three- to nine-membered ring.

12. The process as claimed in any of the preceding claims, wherein metal complexes having central atoms selected from the group consisting of Rh, Ru, Ir, Pd, Pt, Ni, in particular ones containing rhodium as central atom, are used as homogeneous metal atom-ligand complex.

13. The process as claimed in any of the preceding claims, wherein alkyl is an unbranched or branched aliphatic or cyclic hydrocarbon and aryl is an aromatic radical.

14. The process as claimed in claim 13, wherein both alkyl and aryl bear substituents selected independently from among hydrogen, O-alkyl-(C_1-C_8), O-phenyl, phenyl, aryl, fluorine, chlorine, OH, NO_2, Si-alkyl$_3$-(C_1-C_4), CF_3, CN, SO_3H, N-alkyl$_2$-(C_1-C_4), CO-phenyl, COO-

phenyl, COO-aryl-(C_6-C_{10}), CO-aryl-(C_6-C_{10}), PO-phenyl$_2$, PO-alkyl$_2$-(C_1-C_4), PO(O-alkyl(C_1-C_6))$_2$, Si((alkyl)$_3$-(C_1-C_8), where alkyl and aryl are as defined above.

15. The process as claimed in any of the preceding claims which is carried out at a temperature of –40-100°C.

16. The process as claimed in any of the preceding claims in which further additives are used.

17. The process as claimed in claim 16 carried out using phosphine-rhodium complexes in the presence of acids.

18. The process as claimed in any of claims 1 to 15 carried out using phosphinite-rhodium catalysts without the addition of additives.

19. The process as claimed in any of the preceding claims, wherein solvents used are alcohols, water, halogenated hydrocarbons, ethers, aromatic hydrocarbons and mixtures thereof.

20. The process as claimed in any of the preceding claims, wherein the initial hydrogen pressure is from 0.1 to 300 bar.

21. The process as claimed in any of the preceding claims, wherein the catalyst system is used in an amount of from 0.001 to 5 mol%, based on the carbonyl component of the formula (I).